Investigation of dimensional and structural properties of dye aggregates

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Abstract

The structure and size of aggregates formed by the azo-dye "Gelb GA" in aqueous solution was investigated by proton NMR spectroscopy and pulsed-field gradient NMR at concentrations from 0.7 to 30 mM and temperatures from 10 to 70 °C. The strong temperature and concentration dependence of NMR line widths and chemical shifts shows that the aggregates grow in size with increasing concentration and decreasing temperature. The upfield shift of the NMR peaks with increasing aggregate size indicates a p-stacking of the molecules. In particular at low temperature and high concentrations the measured peak intensities are lower than theoretically expected, indicating the existence of very large aggregates, which are too big to be detected by solution-state NMR. Using pulsed-field gradient NMR the diffusion coefficients of the "NMR-visible" fraction of the aggregates were determined. The hydrodynamic radii (R_h) obtained via the Stokes-Einstein equation are in excellent agreement with estimates of R_h based on the line widths. The values of R_h range from 0.7 nm for the monomer to 1.9 nm for the largest aggregates. The latter value corresponds to an aggregation number of 22 or 37, depending on whether loosely packed or compact aggregates are assumed.